

**OXYGEN-REMOVING PRE-PROCESS FOR COPPER  
INTERCONNECT GROWN BY ELECTROCHEMICAL  
DISPLACEMENT DEPOSITION**

**BACKGROUND OF THE INVENTION**

**5 1. Field of the Invention**

The present invention relates to an oxygen-removing pro-process for copper interconnect grown, and more particularly to an oxygen-removing pre-process for copper interconnect grown by electrochemical displacement deposition.

**10 2. Description of Related Art**

The convention methods of copper growth for very large scale integrated circuit (VSLI) and ultra large scale integrated circuit comprises physical vapor deposition (PVD), chemical vapor deposition (CVD), electroplating, electroless deposition, etc., wherein the copper formed by other methods. However, the step coverage of the copper grown in the grooves in the surface of wafer by PVD is not even, and the copper grown by CVD has a good coverage, but not pure such that the copper grown by CVD has a resistance higher than that of the copper grown by PVD. Furthermore, the prescription of dry etching cannot create a reactant with high volatility such that the copper film cannot be etched and formed leading wires on the surface of the wafer. Consequently, major manufacturers use damascene process to grow copper.

However, the damascene process has complicated steps and a

less output such that many manufacturers try to use the method of electroplating and electroless deposition to alter the processes for growing copper on the surface of the wafer because the electroplating and electroless deposition have a economy manufacturing cost. However,

5 the electroplating agent will pollute the environment in which we live and the resistance, the step coverage and the quality of crystal of the grown need to be promoted such that to use the methods of electroplating and electroless deposition to alter the processes of growing copper Is not extensively accepted.

10 The electrochemical displacement deposition (EDD) is provided to grow copper recently. The EDD is provided as a pre-process of electroplating copper and electroless deposition copper to create a seed layer for promoting the quality of crystal and the resistance of the grown copper. However, the copper grown by the method of the EDD has a high

15 resistance and is difficult to be adhered on the surface of the wafer such that an annealing process is necessary to reduce the resistance of the copper film formed by the EDD.

The present invention has arisen to mitigate and/or obviate the disadvantages of the conventional methods for copper interconnect grown.

#### SUMMARY OF THE INVENTION

The main objective of the present invention is to provide an improved oxygen-removing pre-process for copper interconnect grown.

by electrochemical displacement deposition to get a low electric resistance copper.

The achieve the objective, the oxygen-removing pre-process in accordance with the present invention is to remove the oxygen in the 5 reaction solution before displacement and deposition a copper film/conducting wire such that the copper film/conducting wire is grown and ahs a lower electric resistance.

Further benefits and advantages of the present invention will become apparent after a careful reading of the detailed description with 10 appropriate reference to the accompanying drawings.

#### BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is a function view that the effect of the annealing time on the sheet resistance of the copper film formed by the electrochemical displacement reaction, wherein the environment gas during annealing 15 is H<sub>2</sub> and the annealing temperature is kept at centigrade 500 degrees;

Fig. 2 is a flow chart of oxygen-removing pre-process for copper interconnect grown in a accordance with the present invention; and

Fig. 3 is a function view that the resistivities of samples A and 20 B as-deposited form the reaction solutions A with the oxygen-removing pre-process and B with the oxygen-removing pre-process, wherein the resistivities of A after B post-annealing process for 50 minutes is also demonstrated for comparison.

## DETAILED DESCRIPTION OF THE INVENTION

With reference to Fig. 1, hydrogen is injected into a high-temperature furnace that is kept at centigrade 500 degrees for annealing process. As shown in Fig. 1, the resistance of copper film is 5 gradually reduced relative to the processing time such that we can conjecture that the oxygen contained in the copper film will raise the resistance of the copper film. Consequently, it is believed that oxygen is the primary factor deteriorating the resistivity of the copper film. As a result, the quality of the as-deposited copper films is excellent 10 enough and there is no need of further annealing treatment.

With reference to Fig. 2, the oxygen-removing pro-process in accordance with the present invention comprises the following steps.

1. Preparing a Teflon beaker (10) that is high-purity cleaned.
2. Adding one liter deionized water (2) into the beaker (10).  
15 The deionized water is used as a solvent to mixing reaction solution.
3. The beaker (10) with the deionized water (2) is heated by a heater (11) and kept in boiling for two minutes. The beaker (11) is in an opened condition during being heated for  
20 removing the oxygen that is dissolve in the deionized water.
4. Removing the heater (11) from the beaker (10), closing the beaker (10) by a polypropylene film to prevent the oxygen in the air form being dissolved into the solution and

maintaining the beaker (10) about forty minutes for cooling.

- 5 5. Removing the polypropylene film and adding hydrofluoric acid (BOE) for forty milliliters and cupric sulphate ( $\text{CuSO}_4$ ) for four grams into the beaker (10) and stirring the solution with a Teflon stick (13) such that the solution of EDD is finished and almost containing no oxygen.
6. A wafer (3) with a titanium displacement layer (31) is placed in the beaker (10) for eight minutes to execute displacement process.
- 10 7. Take out the wafer (3) and the high quality copper film (32) will form on the surface of the wafer (3.)

The manufacturing processes of the wafer (3) are described as follow.

1. Preparing a Si-chip that is high-purity cleaned.
- 15 2. To grow a wet oxide layer that has a thickness for 1500 Å for insulating in a high temperature stove.
3. To grow a  $\text{Si}_3\text{N}_4$  layer that has a thickness for 500 Å for insulating and anti-corroded by PECVD.
4. To grow a TiN have a thickness for 100 Å for strengthening the adhering effect between the Ti metal layer and the insulating layer by using a sputtering system.
- 20 5. To grow a Ti metal displacement layer by using a sputtering system, the Ti metal displacement layer has a thickness for

3000 Å.

The wafer (3) as manufactured by the above process can get a better effect after the method of EDD in accordance with the present invention.

5        The copper film or the copper conducting wire has a low electric resistance. With reference to the point B in Fig. 3, the average electric resistance of the copper growing by the method of the present invention is  $1.96\Omega\text{-cm}$  that is very close to the ideal value ( $1.67\Omega\text{-cm}$ ) of copper. To compare with the electric resistance of the copper  
10      film growing by the conventional method, the point A in Fig. 3, the electric resistance of the copper growing by the method of the present invention has is greatly lower than that of the copper that grows using the conventional method. Consequently, the annealing process is unnecessary relative to the present invention.

15      Although the invention has been explained in relation to its preferred embodiment, it is to be understood that many other possible modifications and variations can be made without departing from the spirit and scope of the invention as hereinafter claimed.